



FEDERAL REPUBLIC OF GERMANY
GERMAN PATENT OFFICE
PATENT NO. 198 20 756 C1

RECEIVED
1
MAY 07 2003
GROUP 1700

Int. Cl.⁶:

B26 F 1/26
C 25 F 3/02
//H 01 P 1/20
B01J 32/00
35/04

Filing No.: 198 20 756.5-26

Filing Date: May 8, 1998

Date Granted: November 11, 1999

PERFORATED WORKPIECE AND METHOD FOR ITS MANUFACTURE

Inventors: Dr. Volker Lehmann
80689 Munich, DE

Dr. Hans Reisinger
82031 Grünwald, DE

Dr. Hermann Wendt
85630 Grasbrunn, DE

Dr. Reinhard Stengl
86391 Stadtbergen, DE

Dr. Gerrit Lange
81373 Munich, DE

Dr. Stefan Ottow
24114 Kiel, DE

Applicant: Siemens AG
80333 Munich DE

Publications Considered for
Evaluation of Patentability:
DE 42 02 454 C1

1 [Abstract]

2 A silicon substrate features a first region and a second region. In the first region there are
3 pores passing all the way through. In the second region there are pores that do not pass through
4 the substrate. Manufacture of the workpiece is effected by means of electrochemical etching of
5 the pores, by covering the entire surface of the substrate with a mask layer which is structured by
6 photolithography upon the back side of the substrate, and by etching away the bottoms of the
7 pores in the second region, preferably with KOH.

8

9 Description

10 Various technical applications require perforated workpieces, especially as valuable
11 optical or mechanical filters with pore diameters in the micrometer or submicrometer range.
12 These applications are as isoporous membranes, back-flushing filters, laminizers, catalyst
13 carriers, reagent carriers, electrodes for batteries and fuel cells, spinnerets, tube grids, or filters
14 for electromagnetic waves, such as light or microwaves, for example.

15 A method is known for the manufacture of a perforated workpiece from
16 DE 42 02 454 C1, whereby pore diameters in this range can be produced. With this method, in a
17 first surface of a substrate wafer of n-doped, monocrystalline silicon, pits perpendicular to the
18 first surface are formed by electrochemical etching so that a structured layer is obtained. The
19 electrochemical etching takes place in a fluoride-containing electrolyte, wherein the substrate is
20 connected as the anode. When a depth of the pits is reached that corresponds essentially to the
21 thickness of the finished workpiece, the process parameters are changed so that the cross section
22 of the pits increases and the structured layer is detached as a lamina from which the workpiece is
23 formed.

24 Since it is necessary for the manufacture that neighboring pits must grow together, the
25 shape of the manufactured, perforated workpiece corresponds to the shape of the substrate wafer.
26 The perforated workpiece is thus permeated with pores out to the edge. Thus the mechanical
27 strength of the perforated workpiece is limited.

The invention is based on the problem of specifying a perforated workpiece, and also a
method for its manufacture, that will have an increased mechanical strength.

According to this invention, this problem is solved by a perforated workpiece according
to Claim 1 and by a method for its manufacture according to Claim 4. Additional embodiments
of the invention are indicated in the dependent claims.

The workpiece has a substrate of silicon which is divided into a first region and a second
region. In the first region there are pores that pass through the substrate from a first main surface
to a second main surface. The workpiece is perforated in the first region. In the second region
there are pores that emanate from the first main surface and extend into the substrate, but do not

pass through the substrate. Thus, there is solid substrate material underneath the pores in the second region that increases the stability of the perforated workpiece. The perforated workpiece can therefore be assembled with little danger of being destroyed.

The thickness of the substrate in the direction of the depth of the pores is preferably greater in the second region than in the first region.

By the provision of several first regions, various filter regions can be defined, in particular for applications as a catalyst or reagent carrier.

For mounting or assembly of the perforated workpiece, it is better to provide a ring-shaped second region and to locate the first region within the second region. In this case, the solid edge in the second region acts as a frame for the perforated workpiece.

Preferably the perforated workpiece is produced by the application of electrochemical etching. To do this, pores are created in a first main surface of the silicon substrate by electrochemical etching. The depth of the pores is less than the thickness of the substrate. The first main surface and the surface of the pores, and also a second main surface located opposite the first main surface, are all covered with a mask. In the area of the second main surface, the mask layer is structured so that the second main surface is exposed in the first region. By use of a structured mask layer as an etching mask, the substrate will then be etched in the region of the exposed, second main surface at least as far as the bottom of the pores. Then the mask layer is removed so that the pores located in the first region will pass through the substrate from the first main surface to the second main surface.

The mask layer is made preferably of Si_3N_4 or SiO_2 .

Etching of the substrate to form the transiting pores in the first region is preferably implemented with KOH. Thus, in the second region, an edge region with a surface with a <111> orientation is obtained in the area of the second primary surface.

Electrochemical etching is carried out in a fluoride-containing, acidic electrolyte, where the substrate is connected as the anode in an electrolytic cell. Since the substrate is connected as the anode, the minority charge carriers in the silicon migrate to the first main surface in contact with the electrolytes. A space-charge zone forms there. Since the field strength in the area of the recesses in a surface is always greater than outside of it, the minority charge carriers migrate preferentially to those depressions which are present in a statistical distribution in each surface. The result is a structuring of the first main surface. The deeper an initially small unevenness due to the etching is, the more minority charge carriers will move there due to the increased field strength, and thus the etching attack will also be more powerful at this site. The pits will grow in the substrate in the crystallographic <100> direction.

Preferably, an electrolyte with a concentration of 2-10 wt% of HF is used. For the electrochemical etching, a voltage of 1.5-3 V will be applied. This will produce 20 μm pores size. At a substrate doping of 5 $\Omega \text{ cm}$, the diameter of the perforations will preferably be about 2 μm .

To adjust the power density in the substrate, it is preferable to illuminate the second main surface of the substrate during electrochemical etching.

The invention will be explained in greater detail below, based on one embodiment that is illustrated in the figures.

Figure 1 shows a cross section through a substrate which has pores emanating from a first main surface.

Figure 2 shows the cross section through the substrate after structuring of a mask layer to define the first regions and second regions.

Figure 3 shows a cross section through the substrate after etching of the substrate down to the bottom of the pores.

Figure 4 shows a cross section through the substrate after removal of the mask layer.

Figure 5 shows a top view of the workpiece illustrated in Figure 4.

A substrate 1 made of n-doped, monocrystalline silicon with a resistivity of 5 $\Omega \text{ cm}$ is provided with a surface topology on a first main surface 2. This surface topology is composed of depressions which are arranged at regular intervals and are produced by the use of photolithographic processes with alkaline etching. Alternatively, the surface topology can be formed by light-induced, electrochemical etching.

The first main surface 2 of the substrate 1 is placed in contact with a fluoride-containing, acidic electrolyte. The electrolyte has a hydrofluoric acid concentration of 2-10 wt%, preferably 5 wt%. An oxidizing agent, for example, hydrogen peroxide, can be added to the electrolyte in order to suppress the development of hydrogen bubbles on the first main surface 2 of the substrate 1.

The substrate 1 is connected as the anode. A voltage of 1.5-5 V, preferably 3 V, is applied between the substrate 1 and the electrolytes. The substrate 1 is illuminated by ordinary light from a second main surface 3 located opposite the first main surface 2, so that a current density of 10 mA per cm^2 is obtained. During the electrochemical etching, pores 4 are created, starting from the depressions, which run perpendicular to the first main surface 2 (see Figure 1). After an etching time of 4.5 hours, the pores 4 attain a depth of 300 μm , measured from the first main surface 2 in the direction of pore depth, and a diameter of 2 μm . The distance between neighboring pores 4 amounts to 4 μm .

A mask layer 5 of silicon nitride is formed by CVD deposition to a depth of 100 nm. The mask layer 5 covers both the first main surface 2, and also the second main surface 3, as well as the surface of the pores 4.

By means of a mask (not shown) produced by photolithography, and by plasma etching with CF₄/O₂, the mask layer 5 is structured in the area of the second main surface 3 (see Figure 2). The first regions 6 and second regions 7 are thus defined. In the first regions 6 the second main surface 3 is exposed. In the second regions 7, the second main surface 3 is still covered by the mask layer 5. The first main surface 2 and the surface of the pores 4 are likewise fully covered by the mask layer 5.

By etching with KOH at a concentration of 50 wt%, the substrate 1 will then be etched at least as far as the bottom of the pores 4. Etching of the substrate 1 is effected to a depth of 350 µm, measured from the second main surface 3, at a substrate depth of 625 µm. Thus, the surface of the mask layer 5 is exposed in the first regions 6 in the vicinity of the bottom of the pores 4 (see Figure 3). During etching with KOH, the etching attack moves along preferred crystallographic directions, so that edge regions 71 are formed at the edge of the second regions 7 that have a surface with <111> orientation.

By removal of the mask layer 5 with 50 % (by weight) HF, a perforated workpiece is obtained which has transiting pores 4 in the first regions 6 (see Figure 4). The second regions 7, in which the pores do not pass all the way through the substrate 1, are adjacent to the first region 6. The second regions 7 provide stability to the perforated workpiece.

The first regions 6 have different shapes in the different areas of the perforated workpiece (see top view in Figure 5). The first regions 6 can be covered with a number of pores over a large area, for example, in a square or quadrilateral shape, or they can be configured with a row of pores, or they can be covered with pores in another configuration. Due to etching with KOH to expose the bottoms of the pores 4 in the first region 6, the first region 6 is surrounded by the edge region 71 of one of the second regions 7. The geometric shape of the second regions 7 is selected according to stability requirements. It corresponds to bars, a grid, individual windows, a corrugated frame, or identification features.

As an alternative, the mask layer 5 can be formed by thermal oxidation from SiO₂.

Claims

1. Perforated workpiece

— in which a substrate (1) of silicon having a first region (6) and a second region (7) is provided,

— in which there are pores (4) in the first region (6) that pass through the substrate (1) from a first main surface (2) to a second main surface (3),



Fig 1

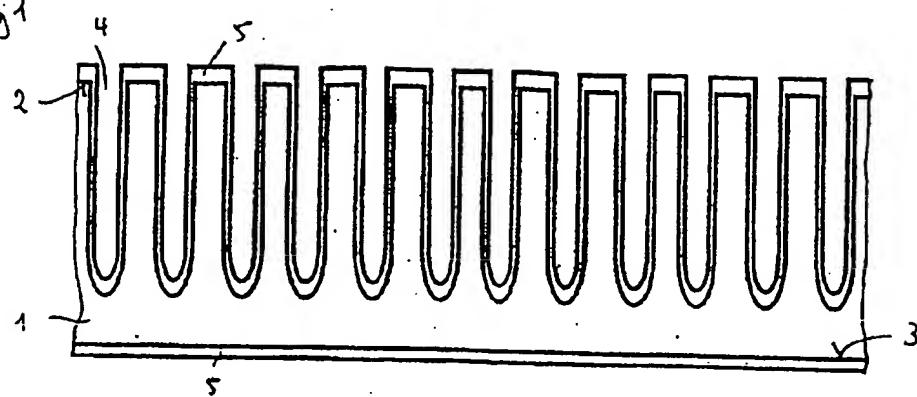


Fig 2

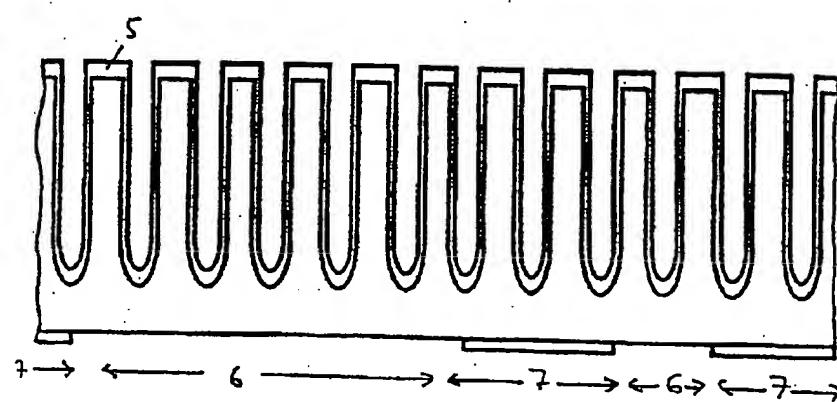


Fig 3

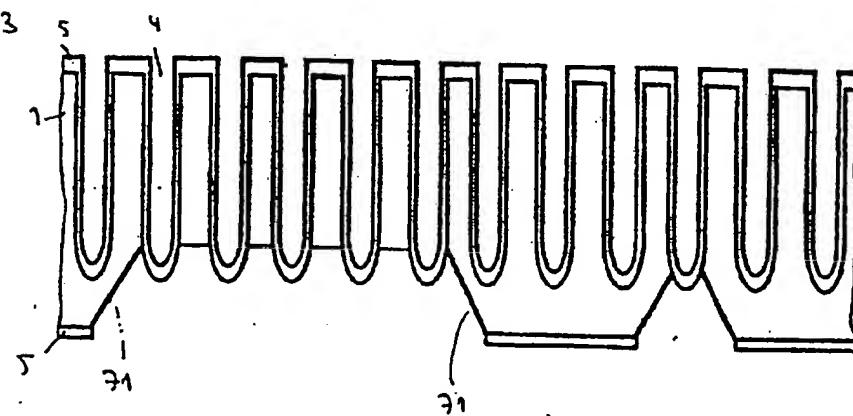




Fig4

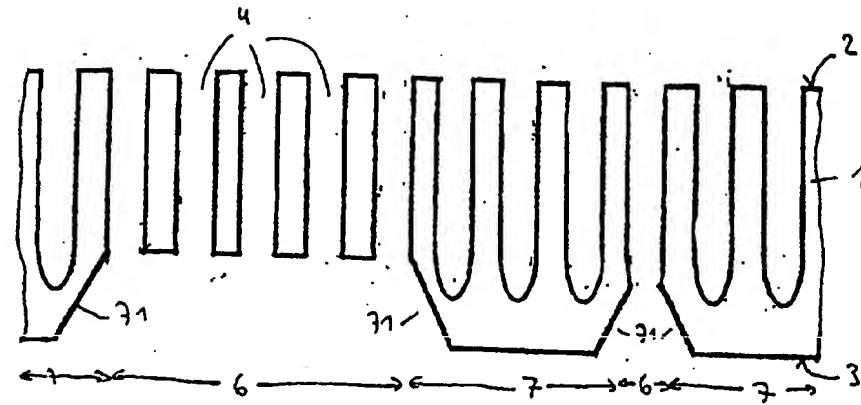


Fig5

